J. of Supercritical Fluids 95 (2014) 265–272

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Catalytic hydrothermal treatment of pharmaceutical wastewater using sub- and supercritical water reactions

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ARTICLE INFO

Article history:
Received 22 November 2013
Received in revised form 22 July 2014
Accepted 23 July 2014
Available online 1 August 2014

Keywords:
Batch reactor
Destruction efficiency
Pharmaceutical compound
Carbamazepine
Metoprolol
Sulfamethaxazole
Sub- and supercritical water
Wastewater treatment

ABSTRACT

Application of subcritical and supercritical water technology for destruction of pharmaceutical compounds (carbamazepine, metoprolol and sulfamethaxazole) was investigated. The experiments were conducted inside batch reactor at a temperature ranging from 473 to 773 K and with different residence times of 5 to 50 min. The results show that carbamazepine, metoprolol and sulfamethaxazole are destructed by 90.27%, 99.99% and 98.84% after a 20 min exposure to 623 K, 673 K and 573 K, respectively. In comparison with the conventional methods of pharmaceutical waste treatment, the current technology provides a higher destruction efficiency (approximately 90–100%) which is achievable in shorter durations. NaOH and $CuSO_4{\cdot}5H_2O$ were also applied as catalysts in the temperature range of 473 K to 723 K. Comparing these catalysts, $CuSO_4{\cdot}5H_2O$ demonstrates a higher destruction efficiency, especially at lower temperatures. Based on the proposed pathway, the products of destructioncan be classified as environmentally-friendly compounds. The results show that this technology can be used as a green alternative for efficient removal of pharmaceutical compounds from wastewater streams.

1. Introduction

The presence of pharmaceuticals in wastewater streams, surface waters, ground waters and related soil environments can have undesirable effects and has therefore attracted a great deal of attention in recent years. As a result,researchers have focused on devising new approaches for wastewater treatment [1–5]. The presence of these organic contaminants in the environment stems from inadequate pharmaceutical compound treatment in wastewater treatment plants (WWTPs) and may lead to chronic changes and ecotoxicity [3].

Many studies have focused on the ineffectiveness of conventional contaminated water treatment facilities. In one study, some β-blockers like metoprolol, propranolol, sotalol and psychiatric drugs such as carbamazepine and hormones were shown to be present in the effluent of a water treatment plant in Spain [3]. Behara et al. studied 5 wastewater treatment plants in South Korea using conventional biological treatment methods and found inefficient removal of 20 pharmaceuticals [2]. Another research on 57 pharmaceutical compounds of 4 wastewater treatment plants in Taiwan showed low removal efficiencies for most drugs, including atenolol, sulfamethoxazole, carbamazepine and metoprolol [4]. There are many other studies elucidating the low removal efficiencies of pharmaceutical compounds such as chloramphenicol, metoprolol, carbamazepine, sulfamethazine, sulfamethoxazole and diazepam [6–8]. The continuous discharge of antibiotics from WWTP and their adverse effects on human health by promoting microbial drug resistance have raised concern about their adverse effects in the environment [9].

An alternative wastewater treatment technology that has gained much attention in recent years is sub-critical and supercritical water technology which is based on the unique behavior of water in its near-critical, critical (T_c = 647.1 K, P_c = 22.1 MPa, ρ_c = 0.322 g/cm^3) and supercritical regions [10]. Raising the self-association of water (k_w) as a result of increasing temperature has severe effects on hydrolysis and acid-base equilibrium; therefore,water can act as an acid or base catalyst precursor because of its high content of H_3O^+ and OH^- ions [10,11]. Increasing temperature also brings about increasing viscosity (η) at gas-like densities and decreasing η at liquid-like densities which result in high fluidity, high molecular mobility and, subsequently, high thermal conductivity of water [10]. Dielectric constant (ε) of water, which shows solvent behavior and ionic dissociation of salts in water, decreases by increasing temperature and decreasing density (a non-polar

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http://dx.doi.org/10.1016/j.supflu.2014.07.017
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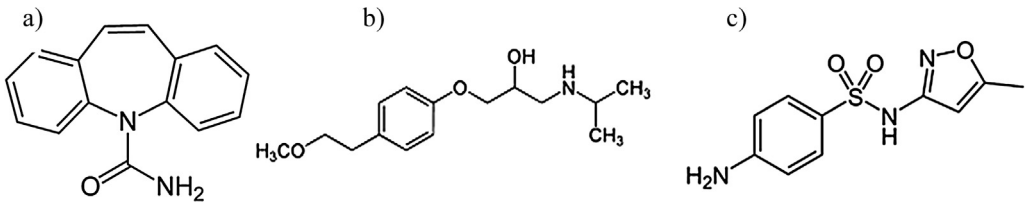

Fig. 1. Chemical structure of (a) carbamazepine, (b) metoprolol and (c) sulfamethoxazole.

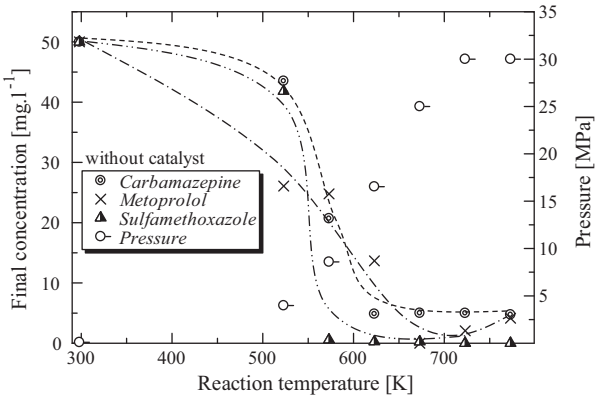

Fig. 2. Effect of temperature and pressure on the final concentration of pharmaceutical compounds at 30 min and with no catalyst.

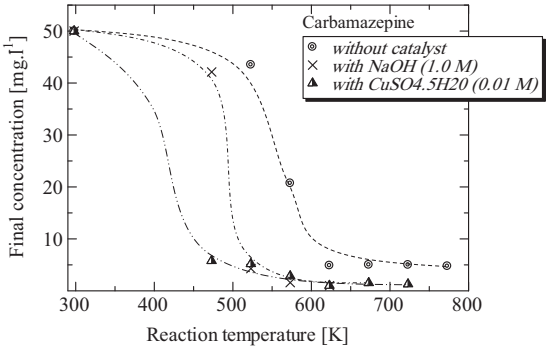

Fig. 4. The comparison of final concentration of carbamazepine in different temperatures with catalyst (NaOH and $CuSO_4{\cdot}5H_2O$) and without catalyst.

state of water), causing an increase in the solubility of hydrophobic organic compounds (HOC) at such conditions [10,12–15]. Briefly, supercritical water is an excellent solvent for homogeneous media without phase boundaries and also provides fast and complete reactions [16,17]. Treatment of some materials such as methane [18–20], methanol [21–25], ethanol [26,27], propane [28], nitrogen [29] and phenol [30–33] has been conducted in subcritical and supercritical water. Furthermore, efficient removal of some compounds including benzene [34], biphenyls [35–39], amines [40,41] and pyridine [42,43] have also been studied in subcritical and supercritical water. Finally, this process can be considered as a green and environmental-friendly technology since it emits no harmful materials to the environment [17,35,39,44,45].

In this study, sub- and supercritical water technology was applied to water contaminated with three pharmaceutical compounds; carbamazepine, metoprolol and sulfamethoxazole, and the effect of changing temperature and time on destruction of these compounds was examined in a batch reactor. Moreover, the effects of potential catalysts, NaOH and $CuSO_4{\cdot}5H_2O$ in destruction efficiency were studied.

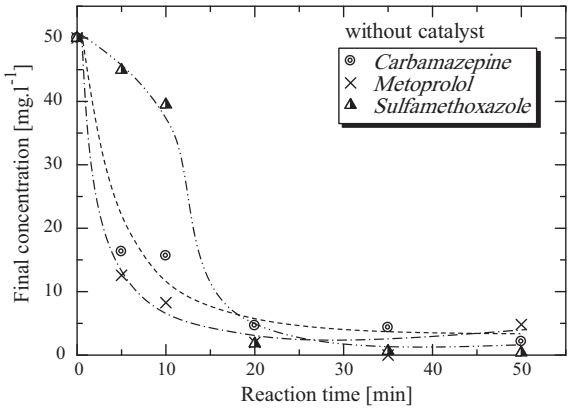

Fig. 3. Effect of residence time on the final concentration of pharmaceutical compounds at 623 K (350 °C) and with no catalyst.

2. Materials and methods

2.1. Chemicals

The 99.8% purified carbamazepine and metoprolol used in this experimental study was obtained from Loghman Co., Pursina Co. and Pars Daroo Co. (Tehran, Iran). Sulfamethoxazolewas was purchased from RoozDaroo Co. (Tehran, Iran). Fig. 1 shows the chemical structure of the above-mentioned compounds. H_2O used throughout the study was distilled and deionized by a laboratory apparatus. Sodium hydroxide (97% pure), copper(II) sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$) (99% pure) were obtained from Merck (New Jersey, USA).

2.2. Experimental apparatus

A tubular batch reactor made of stainless steel 316 SUS (volume 42 mL; length 29.48 cm; i.d. 2.13 cm) was built for this study. Swedgelok caps were used to reach the desired pressure and temperature based on thermodynamic calculations. The aqueous solution containing selected pharmaceutical compounds (initial concentration of 50 mg/L) with an amount of 5.0 to 30.0 mL (based on the pressure and temperature) were charged into the reactor. The reactor was then heated using an electrical furnace. The reactions were conducted in the temperature range of 498 to 773 K and pressure range of 1.5 to 30.0 MPa. After a certain reaction time, the reaction was terminated by immersing the reactor inside ice and water mixture until reaching room temperature.

2.3. Sample preparation

After hydrothermal destruction of pharmaceutical compounds with and without catalyst (NaOH 1.0 M, $CuSO_4{\cdot}5H_2O$ 0.01 M), the liquid content was removed, centrifuged and analyzed. By analyzing different temperatures,the optimum temperature for each compound was determined and consequently, the furnace temperature was set on the optimum temperature for each compound and the experiments were done at various residence times of 5, 10, 20, 35 and 50 min.